Chemical Analyses of the Zeyrek Camii and Kariye Camii Glasses

Robert H. Brill

THE ZEYREK CAMII, the principal church of the Pantokrator monastery in Istanbul, consists of three adjoining structures.[1] The earliest is the building to the south, the church of the Pantokrator, built in 1118–26 by John II Komnenos and Empress Eirene. The building to the north was a church dedicated to the Virgin Eleousa. The two churches were soon joined by a middle building, a funerary chapel dedicated to St. Michael, which served as a mausoleum for the Komnenos family. In the thirteenth century during the occupation of 1204–61, the church was taken over by the Latin rulers, and toward the end of the Byzantine Empire it was the site of additional imperial burials. Shortly after the Ottoman conquest in 1453, the church was converted into a medrese and then into a mosque, at which time it took on the name Zeyrek Camii.

Currently the complex is being repaired and restored in a project led by Robert Ousterhout (University of Illinois) and Zeynep and Metin Ahunbay (Istanbul Technical University). In 1999 the buildings were included in the World Monuments Fund List of 100 Most Endangered Sites. Today the south building still functions as a mosque. In August 1962 I was shown through the south building, originally the church of the

1 Much of the information in this section was drawn from a publication by Robert Ousterhout and his collaborators Z. Ahunbay and M. Ahunbay, "Study and Restoration of the Zeyrek Camii in Istanbul: First Report, 1997–98," *DOP* 54 (2000): 265–70.

Pantokrator, by Cyril Mango, who also showed me some of the glass fragments uncovered there. At that time, the buildings were sadly neglected and dilapidated, but now their condition is much improved. In 1962 I also visited the Kariye Camii, where extensive conservation and restoration work were already underway.

A. H. S. Megaw's Research

During his excavations at the church of the Pantokrator in 1961, A. H. S. Megaw opened two vaults beneath the bema of the church.[2] The vaults contained debris that had apparently been swept into them following destruction accompanying the Ottoman conversion of the building into a mosque. The debris included some coins, the latest of which were dated 1423–48 and 1421–44. It also contained fragments of two rock-crystal cups, bits of enameled gold, and assorted fragments of glass vessels and lamps. Numerous fragments of painted stained-glass windows and pieces of lead came were also found. To all appearances, the stained glass fragments had been swept into the vault along with the other debris in 1453 or shortly thereafter.

Megaw believed that the glass fragments came from borders or other parts of windows that had escaped an initial destruction. He estimated that the fragments represented no more than ten percent of an entire window and suggested that the window could have consisted of panels showing as many as nine life-sized painted figures. His estimate of that percentage might be somewhat high, and scholars have questioned whether nine figures is another overestimate. Nonetheless the finds were extraordinary—and perhaps extraordinarily important. That the fragments came from figural windows cannot be disputed, since one piece shows a well-painted, approximately life-sized eye. In addition, numerous pieces showed painted drapery, arabesques, and rinceaux. Five colors of glass were represented (colorless, dark blue, amber, reddish purple, and green), but no fragments of ruby glass were found. The decorations were definitely fired on. All of the glasses were heavily weathered, and in many instances the paint layers were loose or had become detached.

Megaw made a detailed examination and study of the Pantokrator glasses, looking for parallels among western stained glass windows. The most significant of Megaw's original conclusions was based largely on stylistic features: the windows from which the fragments came had been installed in the church of the Pantokrator at about the time it had been built, that is, circa 1126.[3] Noting that they could have predated even the stained glass windows in the Augsburg cathedral depicting the Prophets—then dated about 1130 and widely regarded as the earliest such windows—this conclusion inevitably raised the question of whether the very idea of painted and leaded stained glass windows might have originated in the eastern Mediterranean and then moved westward. One problem with this hypothesis, however, was that no contemporaneous eastern parallels—at least none of comparable size and sophistication—was apparently known at the time.

Curiously, this startling notion of the possible Byzantine origins of stained glass has never attracted much attention, perhaps because it was soon refuted in a lengthy discourse by the noted expert in the study of stained glass, Jean Lafond.[4] Lafond expressed the view that the Pantokrator glass had been made later, specifically, during the Latin occupation of Constantinople, 1204–61. He was sure that the original figure(s) was executed either by a German glass painter, or at least executed under strong German influence. Hans Wentzel, Louis Grodecki, and Eva Frodl-Kraft, all highly respected authorities on stained

2 A. H. S. Megaw, "Notes on Recent Work of the Byzantine Institute in Istanbul," *DOP* 17 (1963): 333–72.

3 Ibid., 363–64.

4 "Découverte de vitraux historiés du Moyen Age à Constantinople," *CahArch* 18 (1968): 231–38.

glass, also have commented on the Pantokrator windows and mentioned the proposed eastern origin of leaded and painted stained glass windows.[5] No new perspective emerged until 1995, when in a paper on Constantinopolitan glass in general, Julian Henderson and Marlia Mundell Mango reported on chemical analyses of glass from the Kariye Camii.[6]

In 2000 I contacted Megaw regarding the chemical analyses of samples of the Zeyrek Camii glass, including some that he had sent to The Corning Museum of Glass for examination in 1963. The analyses (performed between 1962 and 1976) were to be included in a compendium of analyses then being published by the museum.[7] In his reply, Megaw said that he had since revised his opinion regarding the dating of the Zeyrek Camii window fragments. He remarked: "The stained glass window fragments from Zeyrek Camii, I originally assigned, erroneously, to the construction of the building circa 1126. I accept the opinion of my critics that they belong to a thirteenth century redecoration of the building during the Crusader occupation of Constantinople."[8]

So the question of a date as early as circa 1126 for the Zeyrek Camii windows seemed settled, its major proponent having changed his mind. But the crucial matter of the chemical composition of the glass—and of other laboratory evidence—has not yet been discussed thoroughly in print.[9] Intriguing questions about the creation of the windows remain unanswered.

Chemical Analyses of the Zeyrek Camii Glasses

As a result of my visits to the Zeyrek Camii and Kariye Camii in 1962, Megaw submitted to The Corning Museum of Glass a group of glass fragments from both of the churches as well as sections of lead came from the Zeyrek Camii. (These were in addition to the samples submitted by Cyril Mango in 1962.) The glasses were analyzed quantitatively and the results were published in the compendium referred to above, as well as mentioned in other publications.[10] Some lead isotope analyses and oxygen isotope analyses were also carried out. The results of the chemical analyses of the window glass fragments are especially valuable in two respects. First, the glasses turned out to be soda:lime:silica glasses (Na_2O:CaO:SiO_2) of the type made with plant-ash soda as the source of alkali.[11] Second, several of them contain elevated levels of boron (B_2O_3). The data are reported in tables 1 and 2, and selected pairs of oxides are plotted in figures 1–5.

11 For information on plant-ash soda glasses versus those of the natron type, see R. H. Brill, "Some Thoughts on the Chemistry and Technology of Islamic Glass," *Glass of the Sultans,* ed. S. Carboni and D. Whitehouse (New York, 2001), 25–45, and R. H. Brill in *Serçe Limanı: An Eleventh-Century Shipwreck*, ed. G. F. Bass (College Station, Tex., 2004).

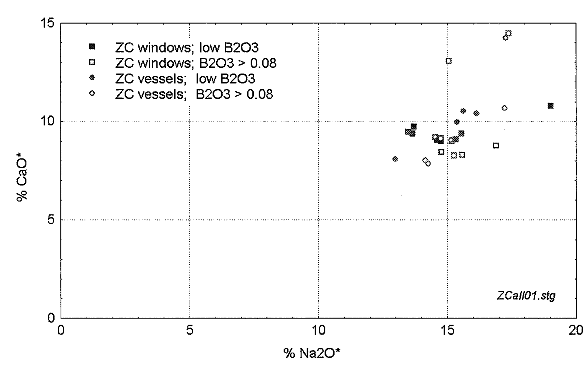

Fig. 1 Graph of lime vs. soda for 28 Zeyrek Camii glasses (18 window fragments and 10 vessel fragments). Asterisks indicate data are for reduced compositions, that is, seven or eight major and minor oxides normalized to 100.0%. Points are plotted smaller than normally required in order to improve legibility (all illustrations by author).

5 Wentzel, "Neue Forschungen zur Glasmalerei des Mittelalters," *Kunstkronik* 17 (1965): 326; Grodecki, "Chronique—Vitrail," *BullMon* 123 (1965): 82–84; Frodl-Kraft, *Die Glasmalerei: Entwicklung, Technik, Eigenart* (Vienna, 1970), 27–28.

6 "Glass at Medieval Constantinople: Preliminary Scientific Evidence," *Constantinople and its Hinterland: Papers from the Twenty-Seventh Spring Symposium of Byzantine Studies, Oxford, 1993*, ed. C. Mango and G. Dagron (Aldershot, Hampshire, 1995), 333–56.

7 R. H. Brill, *Chemical Analyses of Early Glasses*, vol. 1, *Catalogue of Samples*, and vol. 2, *Tables of Analyses* (Corning, N.Y., 1999).

8 He added: "The fragments from Kariye Camii are quite different, and so far as I know, their connection with the first Byzantine decoration of the church has not been challenged. That was in the early 12th century."

9 The glasses have been mentioned on numerous occasions in lectures and teaching sessions, for example at the 8th Colloquium of the Corpus Vitrearum Medii Aevi, York, 27 September 1972.

10 Brill, *Chemical Analyses,* 1:103, 117 and 2:210–12. The analyses reported in this reference, and copied here, were performed by Dr. Brandt A. Rising and his colleagues at Umpire and Control Services, West Babylon, N.Y. between 1962 and 1976. Some of the boron analyses were repeated by analytical chemists at Corning Glass Works. Because of an unfortunate oversight, the name of the Zeyrek Camii was misspelled in the reference cited above. The parent fragments of the samples were very similar to those illustrated in Megaw, "Notes," figs. G–L, pls. 20–22, and color plate facing p. 333 (n. 2 above).

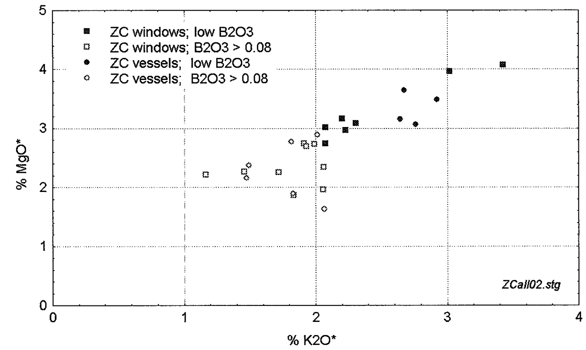

Fig. 2 Graph of magnesia vs. potash for 28 Zeyrek Camii glasses

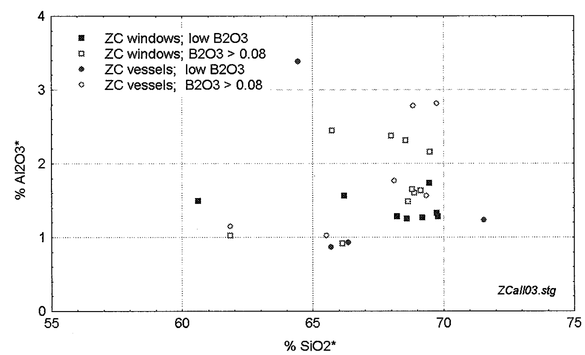

Fig. 3 Graph of alumina vs. silica for 28 Zeyrek Camii glasses

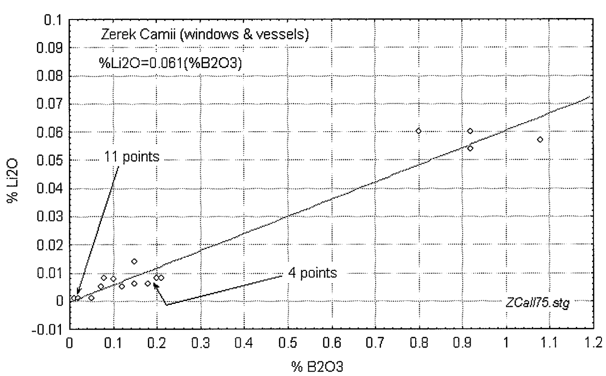

Fig. 4 Graph of Li_2O (lithium oxide) vs. B_2O_3 for Zeyrek Camii glasses

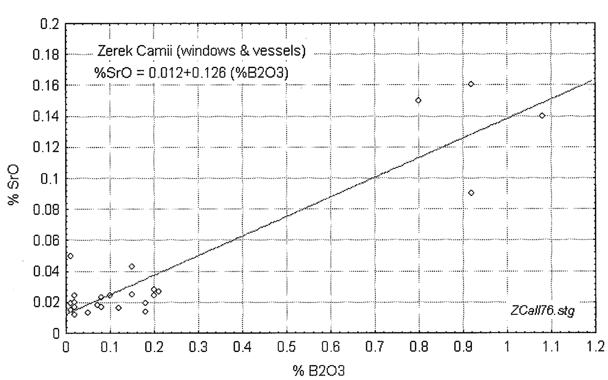

Fig. 5 Graph of SrO (strontium oxide) vs. B_2O_3 for Zeyrek Camii glasses

With the exception of one group of very special glasses, stained glass windows of the twelfth and thirteenth centuries in western Europe appear to be almost invariably potash:lime:silica glasses (K_2O:CaO:SiO_2). The very special exceptions are some dark-blue soda glasses found mixed in among potash glasses of other colors in certain windows. In fact, among some four hundred western European stained glasses analyzed for The Corning Museum, no soda-lime glasses at all were found dating even as late as the fifteenth to sixteenth centuries.[12]

Thus the Zeyrek Camii glasses, being soda-lime glasses instead of potash-lime glasses, are the product of an entirely different glassmaking tradition than that used for making western glasses of roughly contemporaneous dates. I conclude, therefore, that the Zeyrek Camii glasses were not made in western Europe; but there is more.

Among the more than three thousand ancient, Islamic, and western medieval glasses we have analyzed over the past forty years, only two dozen or so have been found that contain more than 0.01–0.02 percent boric oxide (B_2O_3).[13] At this low level, the boron is an accidental impurity from batch materials. However, those two dozen or so exceptional glasses containing higher levels of boron all have connections with Turkey, Cyprus, or Greece.[14] They range in date from the sixth or seventh century to about the twelfth century. In addition to the Zeyrek Camii fragments, they include fragmentary blue beakers, some fragments from Corinth, and both vessel fragments and cullet from Aphrodisias.[15] The elevated boron contents, which range from about 0.08 to just under 1.0 percent, have been confirmed in every case by one or two reruns. The elevated boron levels are still only impurities, but they appear to result from the use of some particular batch material, possibly ashes from plants grown in a region characterized by a soil contamination of boron. For the moment, I do not know where that region is, but it is likely to be in Turkey, perhaps near colemanite deposits. (Colemanite is a boron-containing mineral.) The graphs in figures 4 and 5 illustrate the elevated levels of boron in these glasses and also show that the elevated boron levels are associated with elevated levels of lithium and strontium oxides (Li_2O and SrO respectively.)

I am convinced that the Zeyrek Camii glasses were made in the Byzantine world; and this belief will hold, unless western medieval glasses are found elsewhere that match both the soda-lime composition and its elevated boron impurity. Thus the glass from which the Zeyrek Camii windows were made was itself made not very far from where the windows were found. However, that says nothing about where the window glass was formed, who painted the windows, when and where they were painted, or what inspired their creation. Perhaps none of those questions will ever be answered. According to J. Lafond, the windows might have been painted by a German artist who came to Constantinople for

12 The Jarrow and Wearmouth glasses are excluded from this generalization. Also some mixed-alkali glasses were made early on in southern France. They might have been made from barilla, considering their proximity to the Mediterranean coast. Moreover, although soda-lime glasses are found on the continent from the Middle Ages, some of them were natron-based glasses—in other words, not made from soda derived from plant ashes. Similarly, most Byzantine mosaic tesserae analyzed proved to be natron based.

For stained glass compositions in general, see R. H. Brill, "Composición química de algunos vidrios de la Catedral de León," in *Conservación de vidrieras históricas: Análisis y diagnóstico de su deterioro; Restauración* (Los Angeles, 1997), 114–31; and R. H. Brill and S. Weintraub, "Chemical Analyses of Some Stained Glass Windows in Léon Cathedral," in *Proceedings of the XVIth International Congress on Glass* (Madrid, 1992), 7:143–48; Brill, *Chemical Analyses*, sections 11 A–11 AS in both vols. 1 and 2 (n. 7 above); and R. H. Brill and P. Pongracz, "Stained Glass from St.-Jean-des-Vignes (Soissons) and Comparisons with Glass from Other Medieval Sites," *JGS* 46 (2004): 115–44.

For the dark blue soda glasses, see R. H. Brill and I. L. Barnes, "The Flight into Egypt, from the Infancy of Christ Window (?): Some Chemical Notes," in S. M. Crosby et al., *The Royal Abbey of Saint-Denis in the Time of Abbot Suger (1122–1151)* (New York, 1981), 81; Brill, *Chemical Analyses*, sections 11 D, 11 G, 11 K, 11 P, 11 S, and 11 AS in both vols. 1 and 2; and R. H. Brill, "Chemical Analyses of Some Glasses from Jarrow and Wearmouth," in R. Cramp's publication on the glass from Jarrow and Wearmouth, forthcoming. I believe that before local cobalt sources were being exploited, these distinctive dark blue glasses had been imported from somewhere to the east where soda-lime compositions still prevailed. To further support this, the blue glasses contain antimony. A less likely alternative explanation might be that a large supply of Roman soda-lime glass colored with cobalt had been recycled.

13 Brill, *Chemical Analyses*, passim.

14 For the data, see ibid., 1:67–68, 72–72, and 102–3; 2:112, 129, 208–13, 254–56. For discussion, see R. H. Brill, "Chemical Analyses of Various Glasses Excavated in Greece," in *Hyalos Vitrum Glass, 1st International Conference: History, Technology and Conservation of Glass and Vitreous Materials in the Hellenic World*, ed. G. Kordas (Athens, 2002), 11–19.

15 For the blue beakers, see D. B. Whitehouse, "Two Medieval Drinking Glasses with Gilded and Enamelled Ornament," in *Hyalos Vitrum Glass*, 199–204. See also the references cited above in n. 14. For Aphrodisias glass, see R. H. Brill, "The Scientific Investigation of Ancient Glass," in *Proceedings of the Eighth International Congress on Glass, London* (Sheffield, 1968), 51–52, and references cited above in n. 14.

that purpose. I remain neutral on that aspect of the attributions, and would welcome the opinions of other experts. One authority, Madeline Caviness, who examined some of the fragments several years ago, concluded that they were executed by someone inexperienced in the art of painting glass windows.[16]

16 Personal communication, July 2002.

Regarding the vessel glass fragments, Megaw thought that they did not all necessarily date to the same period as the window glass fragments did and that perhaps some were as late as the fifteenth century. Some of the vessel glasses do, in fact, have appearances distinctly different from one another, and I also believe they were probably made over a range of dates and probably in more than one place. There are fragments of strongly colored aqua glasses in contrast to well-decolorized colorless glasses. There are thick-walled fragments and fragments from very delicate, thin-walled vessels. Many are heavily weathered, but some only moderately so. Table 3 shows that they also differ in their chemical compositions in that six of the ten vessel fragments have elevated levels of boron—two have about 1.0 percent B_2O_3—whereas the other four do not. There appears to be no clear-cut correlation between the vessel types and their compositions. However, those with the elevated boron also have somewhat lower potassium and magnesium contents (K_2O and MgO). Therefore the vessel glasses evidently were made in at least two different places and/or at different times.

The graphs in figures 1–3 show selected data for the Zeyrek Camii glasses. These are the standard graphs I plot for all soda-lime glasses. The following observations can be made. The window glasses appear to be separable into two groups, which, although they are not very different from each other, are nevertheless distinguishable. The glasses with elevated boron have somewhat lower K_2O and MgO contents and also show a tendency toward slightly higher alumina (Al_2O_3) levels. This indicates that the Zeyrek Camii window glasses could have been made at two different times and/or places. However, such separations might have been over considerable distances or measurable in only small numbers of miles; and the times might have been measurable in only days or weeks. There is no chemical way to tell for certain. Also there are no clear chemical differences between the window and vessel glasses among either the high or low boron types. Some of the vessel glasses were therefore made at the same times and places as some of the window glasses.

The Kariye Camii Glasses

We have also analyzed seven fragments of the Kariye Camii window glasses, which were found in a marble-lined loculus in the center of the bema of the main church of the Chora monastery in Constantinople.[17] Megaw, who submitted these fragments for analysis, said that they derive probably from the original early twelfth-century windows of the apse of the church rebuilt by Isaac Komnenos in about 1120. He suggested that these windows and those from the Zeyrek Camii could have come from contemporaneous workshops and speculated that the Kariye Camii windows were set some ten to twenty years before the Zeyrek Camii windows.[18] The data for the Kariye glasses are reported in table 4. In one important way, they resemble the results for the Zeyrek Camii glasses: they are also soda:lime:silica glasses. Therefore the same claims made above for the Zeyrek Camii glasses also apply to them, namely, the Kariye Camii glass was not made in western Europe. It was almost certainly made in Turkey, Cyprus, Greece, or the Middle East. I include the Middle East because the Kariye Camii glasses analyzed, unlike those from the Zeyrek Camii, do not contain elevated levels of boron—the feature believed to be specific to

17 R. Ousterhout, *The Architecture of the Kariye Camii in Istanbul*, DOS 25 (Washington, D.C., 1987), 30–31.

18 See Megaw, "Notes," 365–67, pls. 23–25, and color plate preceding p. 333 (n. 2 above). See also Brill, *Chemical Analyses*, 1:117 and 2:256.

certain glasses associated with Turkey, Cyprus, or Greece. Nevertheless, we are inclined to believe that the Kariye Camii glasses were made probably near the place of manufacture of the Zeyrek Camii glasses, but that they were made with slightly different batch materials that did not contain the boron impurity. The boron impurity may have occurred only in highly localized regions.

The compositions of the Kariye Camii glasses can be distinguished from the Zeyrek Camii glasses according to some of the major and minor components also. Figures 6–8 show the Kariye Camii data (plotted as triangles) superimposed on the data for the Zeyrek Camii glasses. The following observations can be made, in addition to the important fact that none of the Kariye Camii glasses has elevated boron levels: (1) the Kariye window glasses are somewhat higher in CaO and Al_2O_3 than most of the Zeyrek Camii window glasses; (2) the Kariye window glasses have K_2O and MgO contents that resemble those of the Zeyrek Camii vessel glasses that do not have elevated levels of boron; and (3) the Kariye window glasses are somewhat lower in SiO_2 than most of the Zeyrek Camii glasses. As demonstrated solely by the chemical evidence, the Kariye window glasses could have been made in the same place and at the same time as two of the outlying Zeyrek Camii window glasses, no. 1574 and (possibly) no. 1582. These analyses of the Kariye glasses are in agreement with those of J. Henderson and M. M. Mango, as are my conclusions relative to the Kariye Camii glasses.[19]

Regarding the elevated boron levels in the Zeyrek Camii glasses, when they are replotted along with the data for the Byzantine blue beakers alluded to above (those published previously by D. Whitehouse), the compositions are close enough that all these glasses could very well have had a common origin.[20] Recall that the beakers also have elevated boron contents. The Byzantine blue glasses are plotted as crosses in figures 6–8.

19 Henderson and Mango, "Glass at Medieval Constantinople," passim (n. 6 above).

20 Whitehouse, "Two Medieval Drinking Glasses," and also Brill, "Various Glasses."

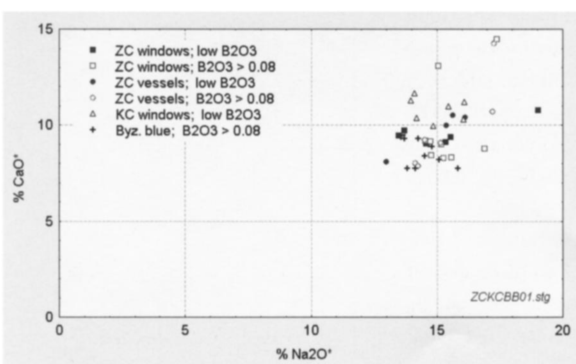

Fig. 6 Graph of lime vs. soda for 7 Kariye Camii window fragments and 9 Byzantine blue vessel fragments superimposed on Zeyrek Camii data

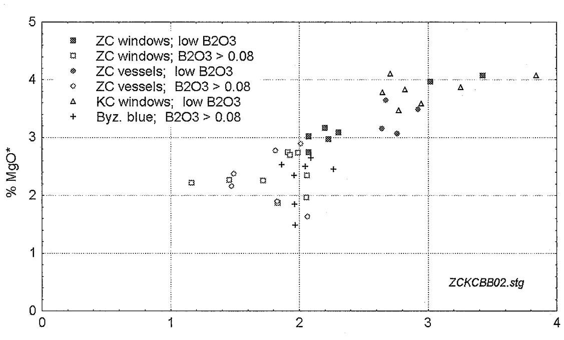

Fig. 7 Graph of magnesia vs. potash for 7 Kariye Camii window fragments and 9 Byzantine blue vessel fragments superimposed on Zeyrek Camii data

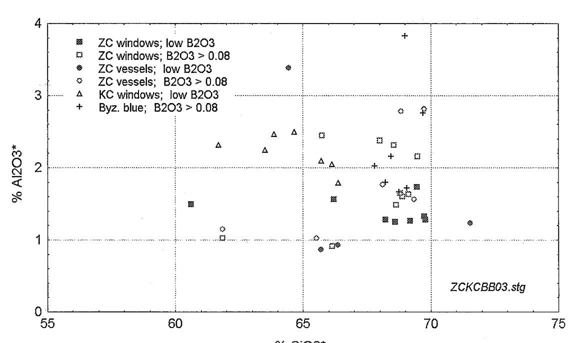

Fig. 8 Graph of alumina vs. silica for 7 Kariye Camii window fragments and 9 Byzantine blue vessel fragments superimposed on Zeyrek Camii data.

Lead Isotope Analyses

Lead isotope analyses of lead extracted from archaeological artifacts can sometimes shed light on the geographic origins of the artifacts themselves, because the isotope ratios of lead in galena ores often vary according to the location of the deposits.[21] By comparing the leads in artifacts with one another, and/or with lead ores, useful similarities and dissimilarities can often be uncovered. The method is not foolproof because there is considerable overlapping of isotope ratios among ores found in different mining regions, and because the salvage and recycling of lead metal in ancient times must sometimes have led to mixing of leads from different sources. Nevertheless such analyses often provide evidence that can be useful if used judiciously.

21 R. H. Brill and W. R. Shields, "Lead Isotopes in Ancient Coins," in *Methods of Chemical and Metallurgical Investigation of Ancient Coinage*, ed. E. T. Hall and D. M. Metcalf, Special Publication 8, Royal Numismatic Society (Oxford, 1972), 279–303.; I. L. Barnes et al., "Lead Isotope Studies of Some of the Finds from the Serçe Liman Shipwreck," in *Proceedings of the 24th International Archaeometry Symposium*, ed. J. S. Olin, M. J. Blackman (Washington, D.C., 1986), 1–12.; R. H. Brill, "Scientific Studies of the Panel Materials," in *Kenchreai, Eastern Port of Corinth*, vol. 2, *The Panels of Opus Sectile in Glass*, ed. L. Ibrahim, R. Scranton, and R. Brill (Leiden, 1976), 227–55. The Corning Museum also has many files of unpublished data.

Lead isotope analyses have been run on lead extracted from several objects recovered from the Zeyrek Camii. The samples were analyzed by Hiroshi Shirahata of the Muroran Institute of Technology in Japan and by I. Lynus Barnes and his associates at the National Institute of Science and Technology in Gaithersburg, Maryland. The samples included nine pieces of lead came, six glasses that contain low levels of lead oxide (PbO), and paints from four fragments of glass. In addition one fragment of glass and three paint samples from the Kariye Camii were also analyzed. The results are reported in table 5 and plotted in figures 9 and 10.

The leads in the six pieces of came from the Zeyrek Camii are of an isotopic type previously associated with a few metallic artifacts from Constantinople. If this association is valid, it is a strong indication that the windows were leaded locally. Figure 9 shows that the leads in the window glasses and paint samples from the Zeyrek Camii are generally similar, although not identical, to those in the cames, thus supporting the chemical evidence that the glasses were manufactured nearby.

However, the leads in the glass fragment and the three paint samples from the Kariye Camii all differ somewhat from the Zeyrek Camii leads. The three Kariye Camii paint samples contain leads that are nearly identical to one another. Isotopically, evident in figure 10, they are more like leads in numerous samples of came from medieval windows in western Europe. That raises the tantalizing possibility that although the Kariye Camii glasses are definitely believed to have been made in the East, the artist who painted them might have used a supply of paint brought from western Europe.

It is also curious that the Kariye Camii glass fragment contains lead that differs from leads in the Zeyrek Camii glasses, which appear to be typical of Constantinople. The Kariye Camii glass is colored with cobalt, so perhaps its lead isotope ratios are characteristic of the source of its cobalt colorant. In that

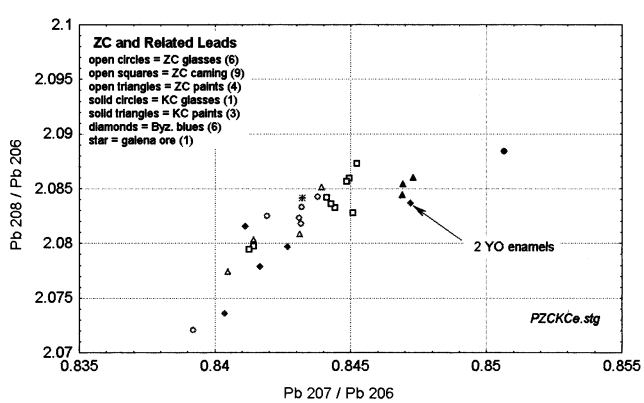

Fig. 9 Lead isotope ratios for lead caming, window glasses, and paints from the Zeyrek Camii and the Kariye Camii. The Zeyrek Camii samples fall within an isotopic range that includes leads from artifacts associated geographically with Constantinople.

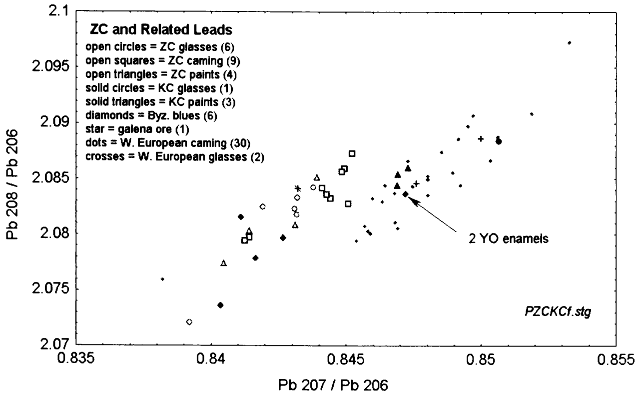

Fig. 10 Lead isotope data for Zeyrek Camii and Kariye Camii samples from figure 9 with superimposed data for lead caming and glasses from Austrian, German, and English stained glass windows. Note that the Zeyrek Camii caming, glass, and paint samples and the Kariye Camii glass sample differ from Western European samples, indicating that their leads came from different geological sources. In contrast, the three paint samples from the Kariye Camii could have come from a western European source. The Byzantine blue samples are from a well-known type of Byzantine glass beaker.

respect the lead in question matches fairly closely the traces of lead in some thirteenth- to fourteenth-century dark blue potash glasses from stained glass windows at Canterbury, Coventry, and Saint-Denis. These were certainly made in western Europe.

Oxygen Isotope Analyses

Oxygen isotope analysis has not been widely applied to the study of ancient glasses. Only one major study has been published.[22] However, the method is informative about the raw materials that were used to make the glasses. Furthermore, it provides information that is independent of chemical composition information. It can even distinguish between glasses that might have identical chemical compositions, if they were made from batch materials that differ in their starting O^{18} contents. (O^{18} is an isotope of oxygen.)

Oxygen isotope analyses were performed on samples of four of the Zeyrek Camii glasses many years ago. It was found that two glasses with an elevated level of boron (nos. 143 and 246) had a markedly different oxygen isotope makeup than did two glasses with low levels of boron (nos. 542 and 543). This confirmed that the two pairs of glasses were made with batch materials from different sources. Additional oxygen isotope analyses of the window glasses from both the Zeyrek Camii and the Kariye Camii might prove very useful.

22 Brill, *Chemical Analyses*, 1:301–22. For earlier publications, see R. H. Brill, "Lead and Oxygen Isotopes in Ancient Objects," in *The Impact of the Natural Sciences on Archaeology*, ed. T. E. Allibone (London, 1970), 143–64; R. H. Brill, "Scientific Studies of Stained Glass," *JGS* 12 (1970): 185–92; and idem, "Scientific Investigations of the Jalame Glass and Related Finds" in *Excavations at Jalame, Site of a Glass Factory in Late Roman Palestine*, ed. G. D. Weinberg (Columbia, Mo., 1988), chap. 9, 257–94.

Conclusions

The chemical analyses firmly establish that the analyzed window and vessel glasses from the Zeyrek Camii and the Kariye Camii were made in the East and were not imported from the West, based on the fact that they are soda-lime glasses, not potash-lime glasses. Furthermore the elevated levels of boron in the Zeyrek Camii glasses point strongly toward manufacture somewhere in Turkey, or possibly in Greece or Cyprus. The data suggest that the Zeyrek Camii glasses might have been made at two different locations, or at the same location at different times. (But if there were two locations, they were not necessarily far apart.)[23] The few oxygen isotope analyses that were carried out are consistent with this finding, but indicate that the batch materials came from different sources, regardless of where the glasses were made.

Chemically the Kariye Camii glasses are not identical to the Zeyrek Camii glasses, but neither are they very different (except that none has elevated levels of boron). A thorough stylistic comparison should be made between the painting on the window fragments from the two buildings to determine just how similar or how dissimilar they are. At the same time, stylistic parallels should be sought among nearly contemporaneous windows in the West, even

23 Robert Ousterhout has informed me of the existence of "a street of glass-makers in Constantinople between the Chalkoprateia church and the Forum of Constantine, mentioned in the Middle Byzantine *Miracles of Saint Photeine*." See A.-M. Talbot, "The Posthumous Miracles of St. Photeine," *AB* 112 (1994): 101 and her article in this volume.

though definitive conclusions may present difficulties, considering the limited number of fragments excavated at the Zeyrek Camii.

Lead isotope analyses confirm that the Zeyrek Camii window glasses were leaded probably locally and that at least some of the colored glasses and paints used for decorating them were made probably in or near Constantinople. Lead isotope analyses of paint from the decoration on three of the Kariye Camii window glass fragments suggest that the lead in the paint may have originated in western European mines.

Unfortunately the laboratory studies can not pinpoint a date of manufacture for the glasses; neither can they tell us precisely when or where the windows were painted, who painted them, or what inspired their creation. According to the laboratory evidence alone, the windows could have been made and decorated any time from Megaw's earliest suggested date of circa 1118–26 onward. Opinions based on archaeological and historical data, although they might vary from one individual to another, should define what ranges of dates are possible and which of them are most plausible.

Clearly, specialists in Byzantine studies should review the archaeological and historical evidence and decide just when conditions would have been conducive to the installation of stained glass windows in the Zeyrek Camii and Kariye Camii.[24] But even so, outside my field, I question the validity of a date during the Latin occupation (1204–61), given that the Venetians were probably more intent on acquiring Constantinople's riches than on enhancing them.[25] Moreover Venetian preeminence in glassmaking is not a factor here because Venice did not, during the interval under consideration, have a conspicuous interest in monumental stained glass windows with painted figures. That interest lay farther north and west. If the windows were installed actually during the occupation, it would probably have been done by someone other than Venetians.

Perhaps Megaw's starting hypothesis that the Zeyrek Camii windows date from approximately 1118–26 should be seriously reconsidered. In any event, further research must take into account not only current thinking about Byzantine history but also all that has been learned during the past four decades about the beginnings of stained glass windows in the West. The dating and stylistic analyses of any western European windows that could reasonably have served as prototypes should be reviewed carefully and objectively before a final conclusion is reached regarding the origins of the Zeyrek Camii and Kariye Camii windows.

—The Corning Musuem of Glass

I am very grateful to Cyril Mango and Peter Megaw for providing the samples for analysis. Many of them came originally from the collection of Dumbarton Oaks. Robert Ousterhout was extremely helpful in supplying information about the Zeyrek Camii. In addition he read through an early draft of this paper and made valuable comments. I also thank Michael Cothren for providing me with the latest information on the dating of early windows in the West, as well as Alice-Mary Talbot for her very helpful editorial comments.

The chemical analyses were performed by Brandt A. Rising of Umpire and Control Services Inc., now the UCS Section of Ledoux & Company, Teaneck, N.J. Some of the boron analyses were rerun by analysts at Corning Glass Works, now Corning Incorporated. The lead isotope analyses were performed by two laboratories: the National Bureau of Standards (NBS), now the National

24 See, e.g., the article by Francesca Dell'Acqua in this volume, and her article, "The Stained-Glass Windows from the Chora and the Pantokrator Monasteries: A Byzantine 'Mystery'?" in *Restoring Byzantium: The Kariye Camii in Istanbul and the Byzantine Institute Restoration*, ed. H. Klein (New York, 2004), 68–77.

25 I thank an anonymous reader who noted that there is "Latin painting in Kalenderhane," i.e., the fresco cycle of St. Francis installed during the Crusader occupation of Constantinople.

Institute of Science and Technology (NIST) in Gaithersburg, Md., and the Muroran Institute of Technology in Japan. The work at the NBS and NIST was conducted under the direction of I. Lynus Barnes and that at the Muroran Institute, under the direction of Hiroshi Shirahata. Shana Wilson assisted in the handling of the data and plotting graphs.

Glass Sample Descriptions

Pb numbers are lead isotope sample numbers and O numbers are oxygen isotope sample numbers. (Some lead isotope samples do not have The Corning Museum of Glass analytical numbers.) The abbreviation w. means "weathered" or "weathering."

Zeyrek Camii windows

132 Aqua
134 Pale amber (same as O-64)
136 Pale purple
137 Pale purple (same as O-63)
139 Dark blue (same as Pb-483)
141 Emerald green (same as Pb-484)
143 Dark blue (same as O-10)
145 Dark blue
147 Dark blue
1574 Aqua
1575 Emerald green
1576 Emerald green
1577 Dark blue
1578 Dark blue
1579 Purple
1582 Pale amber
2504 Blown fragment, apparent diam. ~23 cm; olive, w. scum
2505 As above, apparent diam. ~30 cm; dark blue, moderately w. (same as Pb-1156)
Unnumbered sample, dark blue (same as Pb-479)

Zeyrek Camii vessels

246 Colorless (same as O-66)
541 Pale purplish, lightly w. (same as O-68)
542 Colorless, with slight purplish tinge (same as O-69)
543 Beaker with high kick; colorless, heavily w. (same as O-67)
1570 Vessel with folded rim, dark blue
1571 Lamp stem, solid; aqua, heavily w.
2500 Thin-walled; colorless, w. scum; north vault under bema, to 3.90 m
2501 Thin-walled with pontil mark; aqua, w. scum
2502 Thin-walled, colorless, w. crust
2503 Rim; colorless, w. scum

Kariye Camii windows

149 Dark blue
151 "Orangy" purple
152 Aqua (same as O-70)
154 Amber
156 Emerald green
1580 Purple
1581 Colorless
8299 Dark blue (same as Pb-1059)

Zeyrek Camii paints

142 Paint from no. 141 (emerald green)
144 Spongy black paint from no. 143 (dark blue)
146 Spongy black paint from no. 145 (dark blue)
148 Paint, poss. two colors, from no. 147 (dark blue)
Unnumbered sample, paint from dark blue glass (same as Pb-479W)

Kariye Camii paints

150 Paint from no. 149 (dark blue; same as Pb-485)
153 Paint from no. 152 (aqua)
155 Paint from no. 154 (amber)

Table 1 Zeyrek Camii Windows (Low B_2O_3)

	1574	1582	136	137	1579	147	1577	1578
SiO_2 d	65.08	59.60	67.50	67.60	66.61	67.20	68.94	68.82
Na_2O	15.3	18.7	15.1	14.2	14.2	13.5	13.5	13.3
CaO	9.22	10.6	8.95	8.80	8.65	9.57	9.25	9.33
K_2O	2.97	3.37	2.19	2.02	2.22	2.17	2.05	2.05
MgO	3.90	4.01	2.92	2.67	2.97	3.12	2.98	2.96
Al_2O_3	1.54	1.47	1.23	1.69	1.22	1.26	1.27	1.31
Fe_2O_3	0.30	0.57	0.46	0.35	0.40	1.67	0.80	0.90
TiO_2	0.12	0.12	0.12	0.03	0.1	0.15	0.1	0.1
Sb_2O_5								
MnO	0.50	0.99	1.14	1.50	2.50	0.85	0.80	0.90
CuO	0.01	0.002	0.004	0.01	0.05	0.008	0.01	0.01
CoO	0.01					0.13	0.2	0.2
SnO_2		0.001	0.001	0.01		0.001	0.01	0.01
Ag_2O		0.002	0.003	0.001		0.001	0.001	0.001
PbO	0.01	0.001	0.001	0.01	0.01	0.005	0.05	0.07
BaO	0.01	0.1	0.1	0.05	0.04	0.1	0.01	0.01
SrO	0.015	0.017	0.013	0.05	0.016	0.016	0.019	0.02
Li_2O	0.001	0.001	0.001	0.001	0.001	0.001	0.0013	0.001
B_2O_3	0.01	0.02	0.05	0.01	0.01	0.02	0.01	0.01
NiO			0.005			0.005		
ZnO		0.007	0.005			0.007		
ZrO_2		0.01	0.01			0.01		
P_2O_5	~1	0.41	0.2	~1	~1	0.21		
Reduced compositions								
SiO_2* d	66.19	60.61	68.60	69.45	69.18	68.22	69.78	69.74
Na_2O*	15.56	19.02	15.35	14.59	14.75	13.70	13.66	13.48
CaO*	9.38	10.78	9.10	9.04	8.98	9.72	9.36	9.45
K_2O*	3.02	3.43	2.23	2.08	2.31	2.20	2.07	2.08
MgO*	3.97	4.08	2.97	2.74	3.08	3.17	3.02	3.00
Al_2O_3*	1.57	1.49	1.25	1.74	1.27	1.28	1.29	1.33
Fe_2O_3*	0.31	0.58	0.47	0.36	0.42	1.70	0.81	0.91
B_2O_3*	0.01	0.02	0.05	0.01	0.01	0.02	0.01	0.01
Total*	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* Normalized oxides. The reduced compositions were calculated by normalizing the oxides indicated to 100.00 percent.

Table 2 Zeyrek Camii Windows (Elevated B_2O_3)

	132	134	141	1575	1576	139	143	145	2504	2505
SiO_2 d	66.37	65.79	64.46	65.14	64.60	67.31	68.60	65.13	61.56	64.20
Na_2O	15.2	15	13.8	13.7	13.7	15	14.6	14.4	17.3	16.5
CaO	8.1	13	8.55	8.67	8.65	8.11	8.33	8.55	14.4	8.56
K_2O	2.01	1.16	1.79	1.78	1.87	1.8	1.7	1.83	1.45	2.01
MgO	2.29	2.21	2.57	2.6	2.57	1.83	2.23	2.56	2.26	1.92
Al_2O_3	2.32	0.91	1.5	1.54	1.55	2.27	2.13	1.41	1.02	2.39
Fe_2O_3	1.14	0.5	0.7	0.7	0.75	1.79	1	0.8	0.75	1.9
TiO_2	0.25	0.03	0.05	0.12	0.15	0.08	0.1	0.1	0.12	0.25
Sb_2O_5										
MnO	1.27	0.01	1.2	0.75	1	0.54	1	0.83	0.03	0.53
CuO	0.095	0.01	4.5	4.5	4.5	0.12	0.05	3.95	0.002	0.35
CoO						0.2	0.2	0.05		0.21
SnO_2	0.05	0.01	0.08	0.1	0.11	0.005	0.02	0.01	0.001	0.05
Ag_2O	0.002	0.001	0.005	0.01	0.01	0.001	0.001	0.001	0.001	0.001
PbO	0.2	0.01	0.12	0.25	0.3	0.01	0.15	0.1	0.001	0.3
BaO	0.15	0.01	0.01	0.01	0.01	0.2	0.01	0.02	0.03	0.1
SrO	0.014	0.16	0.028	0.024	0.024	0.017	0.025	0.027	0.15	0.019
Li_2O	0.006	0.054	0.008	0.0078	0.0082	0.008	0.006	0.0081	0.06	0.006
B_2O_3	0.18	0.92	0.2	0.1	0.2	0.08	0.15	0.21	0.8	0.18
NiO	0.01							0.01	0.005	0.01
ZnO	0.012					0.38			0.005	0.4
ZrO_2	0.03									
P_2O_5	0.3	0.22	0.43			0.25	0.39		0.06	0.11
Reduced compositions										
SiO_2*d	67.99	66.13	68.89	69.13	68.80	68.55	69.48	68.64	61.84	65.74
Na_2O*	15.57	15.08	14.75	14.54	14.59	15.28	14.79	15.17	17.38	16.90
CaO*	8.30	13.07	9.14	9.20	9.21	8.26	8.44	9.01	14.47	8.77
K_2O*	2.06	1.17	1.91	1.89	1.99	1.83	1.72	1.93	1.46	2.06
MgO*	2.35	2.22	2.75	2.76	2.74	1.86	2.26	2.70	2.27	1.97
Al_2O_3*	2.38	0.91	1.60	1.63	1.65	2.31	2.16	1.49	1.02	2.45
Fe_2O_3*	1.17	0.50	0.75	0.74	0.80	1.82	1.01	0.84	0.75	1.95
B_2O_3*	0.18	0.92	0.21	0.11	0.21	0.08	0.15	0.22	0.80	0.18
Total*	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* Normalized oxides. The reduced compositions were calculated by normalizing the oxides indicated to 100.00 percent.

Table 3 Zeyrek Camii Vessels

	542	543	2500	2503	246	1571	2501	2502	541	1570
SiO_2 d	70.50	63.74	65.14	64.98	68.28	66.02	65.04	61.19	65.65	67.50
Na_2O	12.8	15.2	16.0	15.3	14.3	14.7	17.1	17.1	13.5	13.8
CaO	7.97	9.85	10.30	10.30	9.06	8.78	10.60	14.10	7.65	7.60
K_2O	2.72	2.89	2.65	2.59	1.79	1.95	1.48	1.46	1.97	1.77
MgO	3.02	3.45	3.61	3.09	2.73	2.80	2.36	2.14	1.56	1.83
Al_2O_3	1.22	3.35	0.86	0.91	1.54	1.71	1.02	1.14	2.65	2.72
Fe_2O_3	0.30	0.40	0.57	0.73	0.60	0.90	0.75	0.75	2.25	1.50
TiO_2	0.02	0.1	0.12	0.18	0.03	0.17	0.12	0.15	0.20	0.23
Sb_2O_5	0.01	0.01			0.01	0.01				0.01
MnO	1.0	0.40	0.50	1.17	1.0	0.90	0.34	0.52	3.63	0.75
CuO	0.01	0.01	0.004	0.03	0.05	0.3	0.001	0.002	0.091	0.5
CoO	0.01	0.01			0.01	0.01				0.2
SnO_2	0.01	0.01	0.003	0.001	0.01	0.05	0.003	0.001	0.03	0.04
Ag_2O	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.003	0.001
PbO	0.01	0.07	0.001	0.001	0.01	0.42	0.001	0.001	0.1	0.28
BaO	0.01	0.01	0.05	0.2	0.01	0.01	0.01	0.01	0.1	0.01
SrO	0.012	0.024	0.02	0.018	0.043	0.023	0.09	0.14	0.016	0.018
Li_2O	0.001	0.0017	0.001	0.001	0.014	0.0073	0.06	0.057	0.005	0.005
Rb_2O	0.01	0.01			0.01	0.01				0.01
B_2O_3	0.02	0.02	0.02	0.02	0.15	0.08	0.92	1.08	0.12	0.072
V_2O_5	0.01	0.01			0.01	0.01				0.01
Cr_2O_3	0.01	0.01			0.01	0.01				0.01
NiO	0.01	0.01		0.005	0.01	0.01		0.005	0.01	0.01
ZnO	0.01	0.01	0.009	0.011	0.01	0.01	0.004	0.006	0.16	0.01
ZrO_2	0.01	0.01	0.01	0.05	0.01	0.01			0.03	0.01
Bi_2O_3	0.001	0.001			0.001	0.001				0.001
P_2O_5	0.29	0.38	0.13	0.41	0.29	1.0	0.10	0.15	0.28	1.0
As_2O_5	0.01	0.01			0.01	0.1				0.1
Reduced compositions										
SiO_2*d	71.54	64.45	65.70	66.36	69.36	68.10	65.52	61.83	68.85	69.74
Na_2O*	12.99	15.37	16.14	15.62	14.52	15.16	17.23	17.28	14.16	14.26
CaO*	8.09	9.96	10.39	10.52	9.20	9.06	10.68	14.25	8.02	7.85
K_2O*	2.76	2.92	2.67	2.64	1.82	2.01	1.49	1.48	2.07	1.83
MgO*	3.06	3.49	3.64	3.16	2.77	2.89	2.38	2.16	1.64	1.89
Al_2O_3*	1.24	3.39	0.87	0.93	1.56	1.76	1.03	1.15	2.78	2.81
Fe_2O_3*	0.30	0.40	0.57	0.75	0.61	0.93	0.76	0.76	2.36	1.55
B_2O_3*	0.02	0.02	0.02	0.02	0.15	0.08	0.93	1.09	0.13	0.07
Total*	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* Normalized oxides. The reduced compositions were calculated by normalizing the oxides indicated to 100.00 percent.

Table 4 Kariye Camii Windows

	152	1581	154	151	1580	156	149
SiO_2 d	65.15	65.33	66.14	62.76	62.68	60.20	63.20
Na_2O	14	13.9	14.8	15.8	13.7	15.7	15.4
CaO	10.2	11.2	9.92	10.1	11.3	10.9	10.9
K_2O	2.78	2.93	2.64	2.66	2.69	3.75	3.24
MgO	3.77	3.56	3.77	4.03	3.36	3.97	3.85
Al_2O_3	2.02	2.08	1.78	2.42	2.42	2.26	2.23
Fe_2O_3	0.6	0.4	0.6	0.5	0.8	0.8	0.7
TiO_2	0.08	0.1	0.13	0.1	0.15	0.13	0.1
Sb_2O_5							
MnO	1.2	0.4	0.1	1.5	2.5	0.1	0.01
CuO	0.01	0.01	0.01	0.01	0.1	2	0.1
CoO							0.1
SnO_2	0.01	0.01	0.01	0.01	0.05	0.01	0.01
Ag_2O		0.001	0.001	0.001	0.001	0.005	0.001
PbO	0.08	0.01	0.01	0.01	0.06	0.08	0.07
BaO	0.01	0.01	0.01	0.02	0.04	0.01	0.01
SrO	0.05	0.03	0.05	0.05	0.1	0.05	0.05
Li_2O	0.002	0.001	0.001	0.002	0.005	0.001	0.001
B_2O_3	0.01	0.01	0.01	0.01	0.01	0.01	0.01
NiO	0.03	0.02	0.02	0.02	0.03	0.02	0.02
ZnO							
ZrO_2							
P_2O_5							
Reduced compositions							
SiO_2*d	66.13	65.72	66.37	63.86	64.65	61.69	63.50
Na_2O*	14.21	13.98	14.85	16.08	14.13	16.09	15.47
CaO*	10.35	11.27	9.96	10.28	11.66	11.17	10.95
K_2O*	2.82	2.95	2.65	2.71	2.77	3.84	3.26
MgO*	3.83	3.58	3.78	4.10	3.47	4.07	3.87
Al_2O_3*	2.05	2.09	1.79	2.46	2.50	2.32	2.24
Fe_2O_3*	0.61	0.40	0.60	0.51	0.83	0.82	0.70
B_2O_3*	0.03	0.02	0.02	0.02	0.03	0.02	0.02
Total*	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* Normalized oxides. The reduced compositions were calculated by normalizing the oxides indicated to 100.00 percent.

Table 5 Lead Isotope Ratios

Pb number	CMG number	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{204}Pb/^{206}Pb$
Zeyrek Camii				
Lead caming				
Pb-971		0.845220	2.087290	0.053914
Pb-973		0.84805	2.08468	0.05379
Pb-974		0.844410	2.083223	0.053999
Pb-975		0.844950	2.085934	0.053929
Pb-258		0.844279	2.083608	0.053999
Pb-259		0.844856	2.085621	0.053940
Pb-78		0.841264	2.079410	0.053824
Pb-970		0.845090	2.082800	0.053870
Pb-972		0.844110	2.084200	0.053860
Glasses				
Pb-479	dk. blue	0.839215	2.072049	0.053648
Pb-483	CMG 139, dk. blue	0.843203	2.083280	0.053832
Pb-484	CMG 141, em. green	0.843097	2.082302	0.053810
Pb-1156	CMG 2505, dk. blue	0.84317	2.08177	0.053883
Pb-3230	dk. green	0.843782	2.084259	0.053830
Pb-3231	bl. green	0.841920	2.082510	0.053425
Paints				
Pb-479W	black	0.840480	2.077370	0.053749
Pb-3232	black	0.843924	2.085116	0.053833
Pb-3233	black	0.841430	2.080300	0.053729
Pb-3234	black	0.843116	2.080871	0.053792
Kariye Camii				
Glasses				
Pb-1059	CMG 8299, dk. blue	0.85066	2.08838	0.054496
Paints				
Pb-485	CMG 150	0.846917	2.085397	0.054212
Pb-3235	gray	0.847306	2.086015	0.054236
Pb-3236	grayish brown	0.846904	2.084443	0.054260
Byzantine blues				
Pb-1018	CMG yellow enam.	0.847210	2.083680	0.054220
Pb-1019	CMG yellow enam.	0.847140	2.083400	0.054241
Pb-1058	CMG dk. blue glass	0.84268	2.07970	0.05389
Pb-1157	Cyprus dk. blue glass	0.840350	2.073580	0.053920
Pb-1158	Corinth dk. blue glass	0.841657	2.077857	0.053827
Pb-1159	Corinth dk. blue glass	0.841124	2.081530	0.0553660
Galena ore				
Pb-118	Yukari Maden Köyü	0.84322	2.08414	0.054019